

PATENT ABSTRACTS OF JAPAN

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(54) SILANIZED, PYROGENICALLY PREPARED SILICIC ACID, ITS PREPARATION AND THICKENER FOR LIQUID

(57)Abstract:

PURPOSE: To obtain a silicic acid useful as a fluidity improving agent and reinforcing filler by treating a pyrogenically prepared silicic acid with a specific compd.

CONSTITUTION: The objective silicic acid is obtained by steps: charging a pyrogenically prepared silicic acid in a mixer, and then spraying a compd. having a group $(RO)_3SiC_nH_{2n+1}$ (R is an alkyl; n is 10-18) following optionally spraying a water of pH 7-1 under vigorous stirring, and after mixing them for 15-30 min., the mixture is thermally treated at a temp. of 100-160°C for 1-3 hrs.

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CLAIMS

[Claim(s)]

[Claim 1]In silanized silicic acid which was manufactured in pyrolysis, manufactured silicic acid in pyrolysis Inside of a basis $(\text{RO})_3\text{SiC}_n\text{H}_{2n+1}$ [type, Silanized silicic acid which processing with a compound which consists of] showing $n=10-18$ and $R=$ alkyl and which was manufactured in pyrolysis.

[Claim 2]The silanized silicic acid according to claim 1 which processed silicic acid manufactured in pyrolysis with a compound of $3(\text{CH}_3\text{O})\text{SiC}_{16}\text{H}_{33}$ (hexadecyl trimethoxysilane) and which was manufactured in pyrolysis.

[Claim 3]The silanized silicic acid according to claim 1 which processed silicic acid manufactured in pyrolysis with a compound of $3(\text{CH}_3\text{O})\text{SiC}_{18}\text{H}_{37}$ (octadecyltrimethoxysilane) and which was manufactured in pyrolysis.

[Claim 4]In a process of silicic acid in which an any 1 paragraph statement of the 3rd paragraph was silanized from claim 1 and which was manufactured in pyrolysis, Insert in in a mixer silicic acid manufactured in pyrolysis, and violently under mixing, responding to silicic acid at necessity -- first -- water -- and post mixing of the consisting [of basis $(\text{RO})_3\text{SiC}_n\text{H}_{2n+1}$] compound being succeedingly sprayed and carried out for 15- 30 minutes, and at temperature of 100-160 ** succeedingly. A process of silanized silicic acid which was manufactured in pyrolysis heat-treating over 1 to 3 hours.

[Claim 5]A thickener for fluids which consists of silanized silicic acid which was manufactured in pyrolysis.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application]This invention relates to the use as the silanized silicic acid, its process, and a thickener.

[0002]

[Description of the Prior Art]By processing the silicic acid manufactured in pyrolysis by dimethyldichlorosilane, it is publicly known to manufacture the silanized silicic acid which was manufactured in pyrolysis (the Germany patent application public presentation (DE-AS) No. 1163784 gazette).

[0003]The $-\text{SiC}_8\text{H}_{17}$ -basis by which the chemical bond was carried out to the surface, The silicic acid which has a trimethylsilyl group or a poly dimethylsiloxane group and which was manufactured in pyrolysis is publicly known (Schriftenreihe Pigmente Nr.11, 15 pages, Ausgabe August 1991).

[0004]

[Elements of the Invention]A subject of this invention silicic acid manufactured in pyrolysis Inside of a basis $(\text{RO})_3\text{SiC}_n\text{H}_{2n+1}$ [type, It is the silanized silicic acid by processing with a compound which consists of] showing $n=10-18$ and $\text{R}=\text{alkyl group}$, for example, a methyl group, an ethyl group, or same thing which was manufactured in pyrolysis.

[0005]As silicic acid manufactured in pyrolysis, silicic acid manufactured from $\text{SiCl}_4 + \text{H}_2$ and O_2 with an elevated-temperature hydrolysis method can be used.

[0006]Especially, silicic acid which has the following physicochemical-characteristics data and which was manufactured in temperature hydrolysis can be used. : [0007]

[Table 1]

第1表

| 水に対する特性 | | エーロジル (AEROSIL) 90 | エーロジル 130 | エーロジル 150 | エーロジル 200 | エーロジル 300 | エーロジル 380 | エーロジル OX 50 | エーロジル TT 600 |
|---|-------------------|--------------------------|---------------|----------------------------|---------------|---------------|----------------|----------------|-----------------|
| 外 観 | | 親水性 | | | | | | | |
| | | 粗い白色粉末 | | | | | | | |
| BETによる表面積 ¹⁾ | m ² /g | 90 ± 15 | 130 ± 25 | 150 ± 15 | 200 ± 25 | 300 ± 30 | 380 ± 30 | 50 ± 15 | 200 ± 50 |
| 第1粒子の平均粒度 | nm | 20 | 16 | 14 | 12 | 7 | 7 | 40 | 40 |
| スタンプ密度 (Stamp[dichte] ²⁾ 普通の物品 密にされた物品 (添加物 "v") | g/l g/l | 約 80 - | 約 50 約 120 | 約 50 約 120 | 約 50 約 120 | 約 50 約 120 | 約 50 約 120 | 約 130 - | 約 60 - |
| 乾燥減量 ³⁾ (100℃で2時間) % 産出製品の放置における (100℃で2時間) % | % % | < 1,0 < 1 | < 1,5 < 1 | < 0,5 ³⁾ < 1 | < 1,5 < 1 | < 1,5 < 2 | < 1,5 < 2,5 | < 1,5 < 1 | < 2,5 < 2,5 |
| pH- 値 ⁵⁾ (4 % 水性分散液) | | 3,6-4,5 | 3,6-4,3 | 3,6-4,3 | 3,6-4,3 | 3,6-4,3 | 3,6-4,3 | 3,8-4,8 | 3,6-4,5 |
| SiO ₂ ⁸⁾ | % | > 99,8 | > 99,8 | > 99,8 | > 99,8 | > 99,8 | > 99,8 | > 99,8 | > 99,8 |
| Al ₂ O ₃ ⁸⁾ | % | < 0,05 | < 0,05 | < 0,05 | < 0,05 | < 0,05 | < 0,05 | < 0,08 | < 0,05 |
| Fe ₂ O ₃ ⁸⁾ | % | < 0,003 | < 0,003 | < 0,003 | < 0,003 | < 0,003 | < 0,003 | < 0,01 | < 0,003 |
| TiO ₂ ⁸⁾ | % | < 0,03 | < 0,03 | < 0,03 | < 0,03 | < 0,03 | < 0,03 | < 0,03 | < 0,03 |
| HCl ⁸⁾ ⁹⁾ | % | < 0,025 | < 0,025 | < 0,025 | < 0,025 | < 0,025 | < 0,025 | < 0,025 | < 0,025 |
| ふるい残分 ⁶⁾ (モックカーによる, 45 μm) | % | < 0,05 | < 0,05 | < 0,05 | < 0,05 | < 0,05 | < 0,05 | < 0,2 | < 0,05 |

1) DIN 66131 を使用

2) DIN ISO 787/XI, JIS K 5101/18 (ふるいにかけない) を使用

3) DIN ISO 787/II, ASTM D 280, JIS K 5101/21 を使用

4) DIN 55 921, ASTM D 1208, JIS K 5101/23 を使用

5) DIN ISO 787/IX, ASTM D 1208, JIS K 5101/24 を使用

6) DIN ISO 787/XVIII, JIS K 5101/20 を使用

7) 105℃で2時間乾燥させた物質に関して

8) 1000℃で2時間灼熱させた物質に関して

9) HCl 含量は灼熱減量の構成要素である

[0008]Such pyrolysis silicic acid is publicly known. ; VINNAKKA Kuchler who these divide and is indicated to the following (Winnacker-Kuechler), HIEMISSHIE techno ROGI (Chemische Technologie and Band3 (1983).) 4. Auflage, 77 pages, and Ur Mance ene SAIKUROPE dee Dare TEHINISSHIEN HIEMI (Ullmanns Encyklopaedie der technischen Chemie and 4. --) [Auflage and (1982)] 21,462 pages of Band(s).

[0009]The silicic acid manufactured in pyrolysis is processed by $(RO)_3SiC_nH_{2n+1}$ [n= 10-18

and R= alkyl group, for example, a methyl group, an ethyl group, or the same thing is expressed among a formula].

[0010]Especially, the following compound can be used.;

Silang I ${}_{3}(\text{CH}_3\text{O})\text{SiC}_{16}\text{H}_{33}$ (hexadecyl trimethoxysilane)

Silang II ${}_{3}(\text{CH}_3\text{O})\text{SiC}_{18}\text{H}_{37}$ (octadecyltrimethoxysilane).

[0011]Silicic acid by this invention inserts in a mixer the silicic acid manufactured in pyrolysis, The compound (organosilane) which attains to silicic acid in water first by a case, and becomes it from basis $(\text{RO})_3\text{SiC}_n\text{H}_{2n+1}$ succeedingly is violently sprayed under mixing, It can manufacture by carrying out post mixing for 15 to 30 minutes, and heat-treating over 1 to 3 hours at the temperature of 100-160 ** succeedingly.

[0012]The used water may acidify to the pH values 7-1 using acid, for example, chloride.

[0013]The used organosilane may melt into the solvent, for example, ethanol.

[0014]Temperature treatment can be carried out in protection gas atmosphere (for example, under nitrogen).

[0015]The silicic acid which was silanized in Silang I by this invention and which was manufactured in pyrolysis has the physicochemical-characteristics data indicated all over the 2nd table. : [0016]

[Table 2]

第2表

| 出発物質 | A 90 | A 130 | A 150 | A 200 | A 300 | A 380 | OX 50 | TT 600 |
|-------------------------------------|---------|---------|---------|---------|---------|---------|---------|---------|
| 第1粒子の平均粒度 [nm] | 20 | 16 | 14 | 12 | 7 | 7 | 40 | 40 |
| BETによる表面積 [m^2/g] | 40-90 | 60-130 | 75-150 | 100-200 | 150-300 | 200-380 | 20-50 | 100-250 |
| スタンプ密度 [g/l] | 40-140 | 40-140 | 40-140 | 40-140 | 40-140 | 40-140 | 40-140 | 40-140 |
| 乾燥減量 [%] | < 2 | < 2 | < 2 | < 2 | < 2 | < 2 | < 2 | < 2 |
| 灼熱減量 [%] | 0,1-10 | 0,1-10 | 0,1-10 | 0,5-15 | 0,5-20 | 0,5-25 | 0,1-10 | 0,5-20 |
| C-含有率 [%] | 0,1-10 | 0,1-10 | 0,1-10 | 0,5-15 | 0,5-20 | 0,5-25 | 0,1-10 | 0,5-20 |
| pH-値 | 3,5-5,5 | 3,5-5,5 | 3,5-5,5 | 3,5-5,5 | 3,5-5,5 | 3,5-5,5 | 3,5-5,5 | 3,5-5,5 |

[0017]Silicic acid by this invention can be used as a thickener in the lacquer which can be diluted with a fluid, for example, water, and resin, for example, an epoxy resin. Silicic acid by this invention can be used for a row as a fluid improving agent and a reinforcing filler all over silicone rubber, gum arabic, cosmetics, and the end of toner powder.

[0018]

[Example]The used silicic acid which was manufactured in pyrolysis has physicochemical-characteristics data indicated all over the 1st table.

[0019]As an organosilane, The compound of general formula $(\text{RO})_3\text{SiC}_n\text{H}_{2n+1}$ of the following is used. : (Silang I) ${}_{3}(\text{CH}_3\text{O})\text{SiC}_{16}\text{H}_{33}$ (Silang II) ${}_{3}(\text{CH}_3\text{O})\text{SiC}_{18}\text{H}_{37}$.

[0020]Silicic acid is inserted in in a mixer and an organosilane is violently sprayed for water

succeedingly first under mixing.

[0021]After spraying is completed, post mixing is further carried out for 15 to 30 minutes, and it heat-treats at 100-160 °C succeedingly for 1 to 3 hours. Heat treatment can be performed also under protection gas, for example, nitrogen.

[0022]Each reaction condition can be grasped from the 3rd table.

[0023]The physicochemical-characteristics data of the obtained silicic acid which was silanized is indicated all over the 3-4th tables.

[0024]

[Table 3]

第3表

| 例 | エーロジル | シラン | シラン量 (g/エーロ ジル 100 g) | 含水量 (g/エーロジ ル 100 g) | エタノール量 (g/エーロ ジル 100 g) | 熱処理時間 (h) | 熱処理温度 (°C) |
|---|-------|--------|-----------------------------|----------------------------|-------------------------------|--------------|---------------|
| 1 | A 200 | シラン II | 15 | 0 | 0 | 2 | 120 |
| 2 | A 300 | シラン I | 1 | 0 | 9 | 2 | 120 |
| 3 | A 200 | シラン I | 2, 5 | 0 | 0 | 2 | 140 |
| 4 | A 200 | シラン I | 20 | 5 | 0 | 2 | 140 |
| 5 | A 200 | シラン I | 10 | 2, 5 | 0 | 2 | 140 |
| 6 | A 200 | シラン I | 5 | 1, 25 | 0 | 2 | 140 |
| 7 | A 200 | シラン I | 2, 5 | 1, 25 | 0 | 2 | 140 |

[0025]

[Table 4]

第4表

| 例 | pH-値 | スタンプ密度 (g/l) | C-含有率 (%) | 表面積 (m ² /g) | 乾燥減量 (%) | 灼熱減量 (%) |
|---|------|-----------------|--------------|----------------------------|-------------|-------------|
| 1 | 4, 8 | 52 | 7, 9 | 127 | 0, 5 | 5, 2 |
| 2 | 4, 3 | 50 | 1, 3 | 253 | 0, 4 | 1, 8 |
| 3 | 4, 4 | 49 | 1, 7 | 176 | 0, 3 | 2, 5 |
| 4 | 4, 6 | 68 | 10, 1 | 116 | 0, 6 | 12, 7 |
| 5 | 4, 5 | 72 | 5, 7 | 144 | 0, 6 | 7, 1 |
| 6 | 4, 7 | 52 | 2, 6 | 167 | 0, 6 | 3, 4 |
| 7 | 4, 5 | 51 | 1, 9 | 171 | 0, 7 | 2, 5 |

[0026]A thickening action is investigated about the silicic acid manufactured by this invention. As a model system, propanol / water-mixture 1:1, the batch 150g, Choose 7.5 g of silicic acid (5 % of the weight) of the measured quantity, and it is made to distribute for 5 minutes using the dissolver (Disolver) by a part for 2500U/, and measures using Brookfield viscometer RVT

(spindle 4). : [0027]

[Table 5]

| 例 | 系もしくはケイ酸 | 粘 度 |
|----|----------------|-------|
| 8 | プロパノール / 水 1:1 | 80 |
| 9 | エーロジル 200 | 200 |
| 10 | 例3による | 400 |
| 11 | 例4による | 14000 |
| 12 | 例5による | 9800 |
| 13 | 例6による | 800 |
| 14 | 例7による | 400 |

[0028]The silanized silicic acid of excel [to thickening of the unsettled start silicic acid A200] by this invention is clear.

[Translation done.]